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The Heterogeneous Chemistry of Acetone in Sulfuric Acid Solutions: Implications for the Upper Troposphere

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Abstract

The uptake of acetone vapor by liquid sulfuric acid has been investigated over the range of 40-87 wt. % H_2SO_4 and between the temperatures of 198 to 300 K. Studies were performed with a flow-tube reactor, using a quadrupole mass spectrometer for detection. At most concentrations studied (40 to 75 wt. %), acetone was physically absorbed by sulfuric acid without undergoing irreversible reaction. However, at acid concentrations at or above 80 wt. %, reactive uptake of acetone was observed, leading to products such as mesityl oxide and/or mesitylene. From time-dependent uptake data and liquid-phase diffusion coefficients calculated from molecular viscosity, the effective Henry's Law solubility constant (H*) was determined. The solubility of acetone in liquid sulfuric acid was found to increase with increasing acid concentration and decreasing temperature. In the 75 wt. % and 230 K range, the value for H* was found to be ~ $2x10^6$ M/atm. This value suggests that acetone primarily remains in the gas phase rather than absorbing into sulfate aerosols under atmospheric conditions.

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Introduction

In the atmosphere photolysis products of acetone, such as methylperoxy and peroxyacetyl radicals, contribute to the formation of odd hydrogen species (HO_x) as well as peroxyacetylnitrate (PAN) through reaction with nitrogen oxides.[1,2] In affecting the concentrations of atmospherically important species (HO_x and NO_x), acetone can significantly influence ozone formation, especially at altitudes in the upper troposphere where it is perhaps the primary source of HO_x.[3-6] Sources of acetone in the atmosphere include secondary reactions of hydrocarbons (the largest source), biomass burning, and direct biogenic and anthropogenic emissions.[1,7] Since acetone appears to be a significant trace gas species with a budget as much as 0.5 – 1.0 ppb in the atmosphere [1,8], it is important to understand homogeneous and heterogeneous processes that influence the amount of available acetone. Although acetone is highly soluble in water, ~30 M/atm at 298 K[9-13], its partition strongly favors the gas phase due to limited cloud water volume, and thus it appears that direct removal by water droplets or rainwater in the upper troposphere may not be a significant sink of acetone.[14]

Heterogeneous reactions on the surface of sulfate aerosols have been shown to enhance ozone depletion through the liberation of reactive chlorine and the removal of nitrogen oxides in the polar stratosphere. [15] In the upper troposphere, sulfate aerosols are mainly composed of between 40-80 wt. % H_2SO_4 and ambient temperatures are in the range of 200-260 K.[16] The effect of sulfate aerosols on removal of gas-phase acetone (physical uptake or reactive uptake), however, has not been studied in detail under atmospheric conditions.[17-19] Nagakura et al. [17] used a spectrophotometric method to study the liquid-phase reaction of acetone and concentrated sulfuric acid and identified mesityl

oxide (MO) as a reaction product. Subsequently, Leisten and Wright confirmed this finding using a cryoscopic technique. [18] Recently Duncan et al. [19] measured a value of ~ 10^8 M/atm at 180 K for the Henry's law solubility of acetone in 75-90 wt. % sulfuric acid and established the reaction mechanism over a wide range of temperatures and acid compositions. To better understand this issue, we have studied the uptake of acetone by liquid sulfuric acid over temperature and acid concentration ranges similar to those found in the upper troposphere and drawn conclusions about the role of sulfate aerosols in atmospheric acetone chemistry.

Experimental Method

Uptake measurements in this experiment were performed using a fast flow-tube reactor coupled with an electron-impact ionization mass spectrometer.[20,21] The schematic of the experimental apparatus is shown in figure 1. The reactor made of Pyrex tubing was 25 cm long with an interior radius of 1.8 cm. The bottom of the reactor was recessed to form a trough (1.9 cm wide and 0.3 cm deep) which held the liquid sulfuric acid. Temperature during experiments was controlled by flowing cold methanol through the outer jacket of the reactor, and was measured by a set of J-type thermocouples. Helium carrier gas was admitted through a sidearm inlet, while acetone in another helium carrier was added by a movable Pyrex injector. Pressures in the reactor were monitored by a high-precision capacitance manometer (MKS Instruments, Model 390 HA, 10 Torr full scale). Typically, a total pressure of 0.420 Torr was used.

Acetone (Fisher Scientific, 99.9 %, Reagent Grade) was used as received without further purification. A sample vial containing the acetone was placed in a methanol/ dry

ice bath in order to control the concentration of acetone available to the system. Acetone purity was further checked by the mass spectrometer. The partial pressure of acetone in the range of (3-7) x 10^{-6} Torr was used in this experiment. Helium (Matheson Gas Company, 99.999 %, Ultrahigh Purity Grade) was used as shipped for both the acetone carrier gas and main flow gas. Sulfuric acid solutions of known compositions were prepared by dilutions of 96.2 wt. % H_2SO_4 (J. T. Baker Chemical Co.) with distilled water. To ensure a constant composition of H_2SO_4, the acid reservoir was changed frequently and the composition of the acid was checked before and after each set of experiments. Such analysis was performed in two ways. Initial tests were done by titration of the acid by a calibrated NaOH solution following experimental runs. After demonstrating the same results as acid-base titration (less than 1 wt. %), the density of the acid solutions were used as a more expedient method to check H_2SO_4 composition.[22]

In the absence of reaction (reactive uptake of acetone is dealt with separately in the results below), the solution of the time dependent uptake in a semi-infinite planar liquid can be given by: [23,24]

$$\gamma_{obs}(t) = \alpha\left[1 - \mathrm{erf}\left(h\sqrt{t/D_l}\right)\right]e^{h^2 t/D_l} \qquad (1)$$

where $h = \alpha\omega/(4RTH^*)$, α is the mass accommodation coefficient, ω is the mean thermal speed of the molecule, R is the gas constant (0.082 L atm mol^{-1} K^{-1}), T is temperature, H* is the Henry's Law solubility constant, D_l is the liquid diffusion constant and erf(x) is the Gaussian error function. Under cases where $h\sqrt{t/D_l} >> 1$ (lower solubility or longer time), this can be approximated as the following: [24,25]

$$\gamma_{obs}(t) \approx \frac{4RTH^*}{\omega}\left(\frac{D_l}{\pi t}\right)^{1/2} \quad (2)$$

Both solutions for the uptake coefficient were tried with all experimental data and used to determine the value for $H^*D_l^{1/2}$.

Determination of uptake coefficient values from the data involves the equation: [21]

$$\gamma_{obs}(t) = \frac{4k_c}{\omega}\left(\frac{V}{S}\right) \quad (3)$$

where V is the volume of the reaction cell, S is the geometric area of the acid reservoir, and k_c is the corrected first-order rate coefficient. This rate coefficient is related to the fractional change of the gas-phase concentration of the acid absorbed molecule, calculated by: [21]

$$k_c = k\,(1 + kD_g/v^2) \quad (4)$$

where D_g is the diffusion coefficient of acetone in He ($D_g = 210/p$ Torr cm^2 s^{-1} at 200 K), and v is the average flow velocity. The observed first order rate, k, is:

$$k = \frac{F_g}{V}\left(\frac{\Delta n}{n}\right) \quad (5)$$

where F_g is the carrier gas flow rate, and $(\Delta n/n)$ is the fractional change in the gas-phase concentration of acetone after exposing to sulfuric acid. Since a symmetrical, cylindrical tube was not used for the uptake coefficient measurements, correction for radial gas-phase diffusion was not taken into account because this correction was considered to be rather imprecise. However, we estimate that the correction is very small, less than 10 %. It is also noted that a temperature dependence of $T^{1.75}$ was used for estimation of D_g at other temperatures.

Two methods were used to estimate of the liquid phase diffusion coefficient. The first method was suggested by Klassen et al.[26] The diffusion coefficient of acetone in liquid sulfuric acid is given by

$$D_l = \frac{c\,T}{\eta} \tag{6}$$

where T is the temperature, η is the viscosity of sulfuric acid, and c is a constant determined from the molar volume of acetone (Le Bas additivity rules). Wilke and Chang [26] empirically determined the value c for the species in liquid sulfuric acid,

$$c = \frac{7.4 \times 10^{-8} (\kappa_{solvent})^{1/2}}{V_A^{0.6}} \tag{7}$$

where $\kappa_{solvent}$ is a solvent dependent empirical factor ($\kappa_{solvent} = 64$) [26] and V_A is the Le Bas molar volume of solute A (acetone) at its normal boiling temperature ($V_A = 74$ cm^3/mol)[28]. We calculated c to be 4.47×10^{-8} for acetone in H_2SO_4. The result for D_l calculated by this method is shown in Figure 2. In general, D_l decreases with decreasing temperature and increasing acid concentration.

For comparison, the diffusion coefficient of acetone in liquid sulfuric acid was also calculated by the cubic cell model [29]

$$D_l = \frac{RT\rho\lambda^2}{6\eta M_{acetone}} \tag{8}$$

and

$$\lambda = \frac{1}{2}\left(d + \left[\frac{xM_{SO_4} + (1-x)M_{H_2O}}{\rho} \right]^{\frac{1}{3}} \right) \tag{9}$$

where ρ is the density of liquid H_2SO_4 and x is the H_2SO_4 mole fraction. $M_{acetone}$, M_{SO_4}, and M_{H_2O} are the molecular weights of acetone, SO_4, and H_2O respectively. The effective molecular dimension (d) was taken to be 0.55 nm for acetone.[22] The cubic cell method generally finds larger values of D_l than the Le Bas Viscosity method by about 20-50 % as shown in Figure 2. Since the cubic cell method assumes the shape of acetone molecules, we believe the method suggested by Klassen et al.[26] is probably more accurate than cubic cell method and the diffusion coefficients derived from the Le Bas viscosity are used in the determination of the Henry's Law solubility constant. It is noted that the square root of D_l is used in the determination of H* and thus the error associated with the procedure of D_l estimation is about 10-20%.

Results and Discussion

Reversible uptake of acetone below 80 wt. % H_2SO_4

Figure 3 shows the results of a typical uptake experiment for the following experimental conditions inside the flow reactor: 50 wt. % H_2SO_4, T = 205.1 K, v = 1168 cm/s, p (acetone) = 3.3 x 10^{-6} Torr, and p (total) = 0.420 Torr. At approximately 1 minute, the acetone inlet is moved 10 cm upstream, exposing the sulfuric acid to the acetone. An initial sharp decrease in the m/e = 58 (acetone parent peak) signal represents the uptake of acetone by the sulfuric acid solution. Over time, the signal recovers as the sulfuric acid saturates, reducing the acetone uptake. Returning the acetone inlet to the fully downstream position produces a sharp increase in acetone, followed by a decay to original signal level. This similarity in shape and total area of the uptake and desorption

curves indicates that acetone uptake in this region is completely reversible. This holds true for acid concentrations up to 75 wt. % at all temperatures studied. Higher concentrations of sulfuric acid produce a different result, which is discussed below.

In a separate experiment we measure the uptake of acetone on the surface of bare Pyrex reactor without H_2SO_4 under similar experimental conditions. The amount of uptake is negligible as compared to that shown in Figure 3. Thus, we conclude that the uptake of acetone is solely due to the solubility into H_2SO_4.

Using the experimental procedures controlled by Eqs. (3) – (5) and discussed in the preceding section, the raw data can be converted into a measure of the uptake coefficient. Fitting of these data provides the next step in solubility determination for acetone on sulfuric acid. Using only the uptake curve from each experiment, functions of uptake coefficient vs. time are developed, as shown in Figure 4. These data can be fit in two ways, as discussed in the experimental section. Each method produces a similar result, with final values for $H^*D_l^{1/2}$ within 10 to 20 % of each other. Further analysis will use only the data from the error function fit, as the final value was less sensitive to the total time of data selected to fit. From this, it is relatively straightforward to determine the effective Henry's Law constant. Values of D_l and H^* for the range of temperatures and acid compositions studied are shown in Table 1. The error limit for H^* values is estimated to be about 50 %, including the uncertainties of γ_{obs} determination (~15 %), the fitting of Eqs. (1) and (2) (~10 to 15 %), and the estimation of liquid-phase diffusion (~10 to 20 %).

Figure 5 shows the values of H* as a function of 1/T. Also included in this graph are the averaged values for Henry's law solubilities of acetone in water [9-13], extrapolated from higher temperature data in literature. This set of data is used to provide a general reference to our data in liquid sulfuric acid. Two observations can be drawn from this figure. First, the value for H* is shown to increase as the temperature decreases. This is consistent with physical solubility of the acetone in the sulfuric acid solutions. More importantly, the solubility of acetone is found to increase with increasing acid concentration. The weak base nature of acetone would be expected to produce such a reaction if protonation occurs with uptake [30]. Initial protonation during the uptake is reversible within the range of 40 - 75 wt.% H_2SO_4.

For any given acid composition, the temperature dependence of the Henry's Law constant is given by the equation:

$$\ln(H^*) = -\Delta H/RT + \Delta S/R \qquad (10)$$

the ΔH and ΔS are the enthalpy and entropy associated with solvation, respectively. From the linear fits of the data shown in Figure 5, the values for ΔH and ΔS are shown in Table 2. The enthalpy of solvation is found to be nearly independent of acid concentration over the range examined. The entropy of solvation ΔS, however, is shown to generally increase as the concentration of H_2SO_4 increases and can be considered to consist of two terms, ΔS^0 and S^{ex}. ΔS^0 is the entropy of solvation in water and S^{ex} arises for solutions containing sulfuric acid. Because of the limited temperature range of our data, caution must be made to derive S^{ex} from Table 2.

In order to express acetone solubility as a function of temperature and sulfuric acid concentration, we use an empirical equation: [32,33]

$$\ln(H^*) = \ln [K_{H(T_0)}] - mH_2SO_4 f + (\Delta H_0/R)(1/T_0 - 1/T) \quad (11)$$

where $\ln [K_{H(T_0)}] = 3.00$, $\Delta H_0/R = -4850$ (K), $T_0 = 298.15$ K, mH_2SO_4 is the molality of H_2SO_4, and $f = -0.23 + 5.0/T$. The first and third terms relate to the solubility of acetone in water while the second term directly expresses the contribution of sulfuric acid. Initial values for the "f" term were derived from least squares fits of the individual data sets (excluding the extrapolated water values), then adjusted to produce the optimum fit of all of the data. Figure 6 shows the resulting fit of the calculated values to experimental data. Although Eq.(11) fits the data reasonably well, however, care should be taken to extrapolate to the temperature and acid composition outside the ranges we used in this study.

Reactive acetone uptake above 80 wt. % H_2SO_4

The behavior of acetone uptake at and above 80 wt. % H_2SO_4 diverges from what has been observed below this concentration. Figure 7 shows the results of uptake experiments at (a) 80 wt. % H_2SO_4 at 260 K and (b) 87wt. % at 275 K. The horizontal line represents the baseline level of acetone during the experiment. In contrast to figure 3, after initial exposure to sulfuric acid acetone signal does not recover to the baseline acetone level. Additionally, the area under the uptake curve does not match the area under the desorption curve. This indicates that above 80 wt. %, the uptake of acetone is not completely reversible, and may contain a reactive component. It should be noted that

sulfuric acid concentrations of 85 and 87 wt. % (Figure 7b) were also tested, but showed no recovery from exposure of acetone to the acid.

As stated above, the initial uptake in sulfuric acid involves protonation of the weakly basic acetone. Deno and Wisotsky [30] reported 50 % protonation for 81 wt. % H_2SO_4. Reactions on sulfuric acid below 75 wt. % show that this protonation is reversible. Therefore further reaction in sulfuric acid is indicated to produce the results shown in Figure 7.

We have conducted a series of experiments by mixing liquid acetone with H_2SO_4 from 80 to 96 wt. % at room temperature and monitoring reaction products mass spectrometrically. Figure 8 shows the results for 96 wt. % at 295 K. Both mesityl oxide (MO; m/e = 98 amu) as a major product and mesitylene (trimethylbenzene or TMB; m/e = 120 amu) as a minor product are present.[33] For 85 wt. % H_2SO_4 (not shown), only mesityl oxide is observed. These results are consistent with those reported by previous investigations.[17-19, 36] A possible reaction diagram for acetone reaction with sulfuric acid is shown in Figure 9. In principle, an acetone dimer reaction in sulfuric acid forms mesityl oxide while the trimer reaction produces mesitylene.

Comparison with Previous Data

Duncan et al. [19] report a value of $H^* \sim 10^8$ M/atm for acetone in 75 to 90 wt. % sulfuric acid at 180 K. If we extrapolate our data to 180 K in 75 wt. % acid solution, we get a value of 5×10^8 M/atm. Very recently using a Knudsen cell reactor, Klassen et al.[36] report the Henry's Law solubility constant for acetone in 48 to 68 wt. % H_2SO_4 between 210 K and 240 K and use Eq.(2) for data analysis. Their results are about a factor of 2 or 3 smaller than ours. In view of uncertainties associated with the estimated liquid-phase

diffusion coefficients of acetone in H_2SO_4, the determination of γ, and the fitting of Eqs. (1) and (2), we consider these measurements to be in reasonable agreement.

Atmospheric Implications

Using the Henry's law solubilities determined in this work, we can determine the expected impact of sulfate aerosols on upper tropospheric acetone. Assuming typical atmospheric conditions of 75 wt. % H_2SO_4 at 230 K, the value of H* is found to be ~2 x 10^6 M/atm as shown in Table 1 and Figure 5. Under quiescent atmospheric conditions, the volume fraction of sulfate is ~10^{-14} (under volcanic perturbation such as Pinatubo, however, this value may be as high as ~10^{-11}).[37] The ratio of acetone in gas and liquid phases can be represented by:

$$\text{Ratio} = H^*LRT \qquad (12)$$

where L is the volume fraction of sulfate in the upper troposphere as discussed above. These volume fractions, coupled with the expected solubility of acetone in sulfuric acid, suggests that uptake by sulfate would account for only ~ 4 x 10^{-7} of total tropospheric acetone. Even under high sulfate perturbation, such uptake would account for only ~ 4 x 10^{-4} of the atmospheric acetone. On the basis of this information, we conclude that uptake by sulfate is not a significant sink of acetone in the upper troposphere and thus the majority of acetone remains in the gas phase. It is further noted that the possibility of mesityl oxide (MO) formation by the reaction of acetone with sulfate aerosols in the upper troposphere is expected to be also negligible.

Conclusions

In this paper we have reported the uptake of acetone by liquid sulfuric acid over the range of 40 to 87 wt. % H_2SO_4 and between the temperatures of 198 to 300 K. Acetone was found to be physically absorbed by sulfuric acid without undergoing irreversible reaction below acid concentrations of 80 wt. %. Above this acid concentration reactive uptake of acetone formed condensation products such as mesityl oxide. The effective Henry's Law solubility constant (H*) was found to increase with increasing acid concentration and decreasing temperature. Under typical upper tropospheric conditions, we conclude that acetone remains in the gas phase.

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References and Notes

(1) Singh, H. B., et al. *J. Geophys. Res.* **1994**, *99*, 1805.

(2) Singh, H. B.; Kanakidou, M.; Crutzen, P. J.; Jacob, D. J. *Nature* **1995**, *378*, 50.

(3) Wennberg, P. O., et al. *Science,* **1998**, *279*, 49.

(4) Jaegle, L., et al. *Geophys. Res. Lett.* **1998**, *25*, 1709.

(5) McKeen, S. A., et al. *Geophys. Res. Lett.* **1997**, *24*, 3177.

(6) Muller, J.-F.; Brasseur, G., *J. Geophys. Res.* **1999**, *104*, 1705.

(7) Holzinger, R., et al. *Geophys. Res. Lett.* **1999**, *26*, 1161.

(8) Arnold, F., et al., *Geophys. Res. Lett.* **1997**, *24*, 3017.

(9) Snider, J. R.; Dawson, G. A. *J. Geophys. Res.* **1985**, *90*, 3797.

(10) Zhou, X.; Mopper, K. *Environ. Sci. Technol.* **1990**, *24*, 1864.

(11) Betterton, E. A. *Atmos. Environment* **1991**, *25A*, 1473.

(12) Duan, S. X., et al. *J. Phys. Chem.* **1993**, *97*, 2284.

(13) Benkelberg, H. J.; Hamm, S.; Warneck, P. *J. Atmos. Chem.* **1995**, *20*, 17.

(14) Chatfield, R. B.; Gardner, E. P.; Calvert, J. G. *J. Geophys. Res.* **1987**, *92*, 4208.

(15) "Scientific Assessment of Ozone Depletion: 1994", World Meteorological Organization, Global Ozone Research and Monitoring Project-Report No. 37, Chapter 3.

(16) Steele, H. M.; Hamill, P. *J. Aerosol Sci.* **1981**, *12*, 517.

(17) Nagakura, S.; Minegishi, A.; Stanfield, K., *J. Amer. Chem. Soc.* **1957**, *79*, 1033.

(18) Leisten, J. A.; Wright, K. L. *Proc. Chem. Soc.* **1964**, 3173.

(19) Duncan, J. L.; Schindler, L. R.; Roberts, J. T. *Geophys. Res. Lett.* **1998**, *25*, 631.

(20) Leu, M.-T.; Timonen, R. S.; Keyser, L. F.; Yung, Y. L. *J. Phys. Chem.* **1995**, *99*, 13203.

(21) Choi, W.; Leu, M.-T. *J. Phys. Chem.* **1998**, *102*, 7618.

(22) Handbook of Chemistry and Physics, 65th Edition, CRC Press, 1984.

(23) Danckwerts, P.V. *Trans. Farad. Soc.* **1951**, *47*, 1014.

(24) Zhang, R.; Leu, M.-T.; Keyser, L. F. *J. Phys. Chem.* **1997**, *101*, 3324.

(25) Kolb, C. E., et al. in "Progress and Problems in Atmospheric Chemistry", J. R. Barker (Editor), World Scientific Publication, Singapore,1995.

(26) Klassen, J. K; Hu, Z.; Williams, L. R. *J. Geophys. Res.* **1998**, *103*, 16197.

(27) Wilke, C. R.; Chang, P. *ALCHE J.* **1955**, *1*, 264.

(28) Reid, R.C.; Prausnitz, J. M.; Poling, B.E. *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1987.

(29) Houghton, G. *J. Chem. Phys.* **1964**, *40*, 1628.

(30) Deno, N. C.; Wisotsky, M. J. *J. Amer. Chem. Soc.* **1963**, *85*, 1735.

(31) Danckwerts, P. V., *Gas-Liquid Reactions*, McGraw-Hill Book Company, New York (1970).

(32) Huthwelker, T. et al. *J. Atmos. Chem.* **1995**, *21*, 81.

(33) Leu, M.-T.; Zhang, R. *Geophys. Res. Lett.* **1999**, *26*, 1129.

(34) Stein, S. E., director, "IR and Mass Spectra" by NIST Mass Spec Data Center, *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, W.G. Mallard and P.J. Linstrom (Editor), November 1998, National Institute of Standards and Technology, Gaithersburg MD, 20899.

(35) Liler, M. *Reaction Mechanisms in Sulphuric Acid and Other Strong Acid Solutions*, Academic Press, New York, 1971.

(36) Klassen, J. K.; Lynton, J.; Golden, D. M.; Williams, L. R. *J. Geophys. Res.* **1999**, submitted.

(37) "Scientific Assessment of Ozone Depletion: 1998", World Meteorological Organization, Global Ozone Research and Monitoring Project-Report No. 44, Chapter 3.

Table 1. Summary of the effective Henry's Law solubility constants, H*, for acetone in H_2SO_4 (40 to75 wt. %). The error limit for H* values is about 50%.

wt. %	T (K)	$H^*\sqrt{D_l}$	D_l (cm^2/s)	ln H*
40.0	204.1	24.96	4.78E-08	11.65
	207.1	17.32	6.90E-08	11.10
	210.1	12.41	9.68E-08	10.59
	215.1	10.74	1.61E-07	10.20
	216.1	7.73	1.76E-07	9.82
	217.1	9.11	1.93E-07	9.94
	218.1	8.12	2.11E-07	9.78
	218.1	15.19	2.11E-07	10.41
	218.1	8.26	2.11E-07	9.90
	219.1	9.75	2.30E-07	9.92
	220.1	6.46	2.51E-07	9.47
	225.1	9.03	3.73E-07	9.60
	228.1	8.2	4.63E-07	9.40
50.0	198.1	73.53	1.48E-08	13.31
	198.1	76.36	1.48E-08	13.35
	201.1	101.16	2.31E-08	13.41
	203.1	118.62	3.02E-08	13.43
	204.1	81.39	3.43E-08	12.99
	205.1	81.48	3.89E-08	12.93
	206.1	90.53	4.39E-08	12.98
	210.1	67.34	6.90E-08	12.45
	211.1	63.08	7.66E-08	12.34
	212.1	59.28	8.49E-08	12.22
	215.1	47.87	1.14E-07	11.86
	218.1	36.84	1.49E-07	11.47
	218.1	45.24	1.49E-07	11.67
	220.1	27.76	1.77E-07	11.10
	223.1	21.6	2.25E-07	10.73
	228.1	15.34	3.24E-07	10.20
65.0	200.1	357.83	2.42E-09	15.80
	204.1	212.36	5.19E-09	14.90
	206.1	258.88	7.29E-09	14.92
	206.1	166.91	7.29E-09	14.49
	207.1	196.82	8.57E-09	14.57
	210.1	222.64	1.35E-08	14.47
	212.1	195.2	1.78E-08	14.20
	215.1	88.53	2.61E-08	13.21
	216.1	157.78	2.95E-08	13.73
	219.1	127.24	4.15E-08	13.34
	221.1	75.56	5.13E-08	12.72
	222.1	140.33	5.69E-08	13.29

	225.1	112.83	7.61E-08	12.92
	228.1	84.52	9.96E-08	12.50
	231.1	62.41	1.28E-07	12.07
	234.1	62.85	1.62E-07	11.96
	239.1	59.99	2.31E-07	11.73
	251.1	16.87	4.79E-07	10.10
	256.1	26.51	6.20E-07	10.42
	262.1	14.1	8.24E-07	9.65
	266.1	11.71	9.82E-07	9.38
75.0	209.1	552.51	6.98E-10	16.86
	211.1	539.57	1.13E-09	16.59
	214.1	445.95	2.18E-09	16.07
	217.1	322.56	3.88E-09	15.46
	221.1	262.44	7.64E-09	14.92
	223.1	257.91	1.03E-08	14.75
	227.1	223.96	1.80E-08	14.33
	229.1	188.76	2.30E-08	14.03
	250.1	204.82	1.62E-07	13.14
	259.1	93.59	2.92E-07	12.06
	261.1	213.96	3.29E-07	12.83
	262.1	50.14	3.48E-07	11.35
	273.1	137.49	6.12E-07	12.08
	286.1	56.71	1.06E-06	10.92
	292.1	31.83	1.33E-06	10.23

Table 2. Calculated values of ΔH and ΔS for acetone uptake in sulfuric acid using Eq. (10). The uncertainties represent standard errors of measurements.

wt % H_2SO_4	ΔH (kJ/mol)	$\Delta S^0 + S^{ex}$ (J/mol K)
0	-38.1 ± 1.0	-99.6 ± 3.1
40.0	-35.6 ± 4.5	-80.2 ± 20.6
50.0	-40.7 ± 2.4	-91.4 ± 11.4
65.0	-40.8 ± 1.3	-75.2 ± 5.6
75.0	-37.7 ± 2.1	-43.0 ± 8.9

Figure Captions

Figure 1. Schematic of the fast flow-tube reactor. Detection was performed with an electron impact ionization mass spectrometer. Sulfuric acid samples were held in a shallow depression in the bottom of the reactor. Exposure of acetone to sulfuric acid was controlled by a movable glass inlet.

Figure 2. Comparison of the calculated values of D_l from Le Bas additivity and cubic cell methods.

Figure 3. Representative acetone profile as a function of temperature in a typical experiment. Example shown is 50 wt. % H_2SO_4 at 205.1 K. Similar profiles are observed for H_2SO_4 concentrations between 40 and 75 wt. %.

Figure 4. Uptake coefficient of acetone on 50 wt. % H_2SO_4 at 205.1 K as a function of time (upper panel). Solid curve represents the fit of the data to eq. (1), yielding a value for $H^*D_l^{1/2}$. The lower panel shows a similar plot, with the $1/\gamma$ vs. $t^{-1/2}$. The value of $H^*D_l^{1/2}$ in this panel was calculated by eq. (2)

Figure 5. Measured values of H* plotted against inverse temperature for 40 to75 wt % H_2SO_4. Calculated values for supercooled water are shown for comparison. Solid lines are linear fit of the data.

Figure 6. Similar to Figure 5, except the lines shown are calculated from the empirical fit using eq. (11).

Figure 7. Representative acetone profile as a function of temperature for reactive uptake experiment. Examples shown are (a) 80 wt. % H_2SO_4 at 260 K and (b) 87 wt. % at 275 K. The horizontal line indicates level of initial acetone prior to exposure to the acid.

Figure 8. Mass spectrum of desorbing products from liquid acetone reacting with 96 wt. % H_2SO_4. Both mesityl oxide (MO; major product) and mesitylene (TMB; minor product) are identified.

Figure 9. Schematic of the reaction mechanism for acetone with sulfuric acid forming MO and TMB at various concentrations. See text for details.

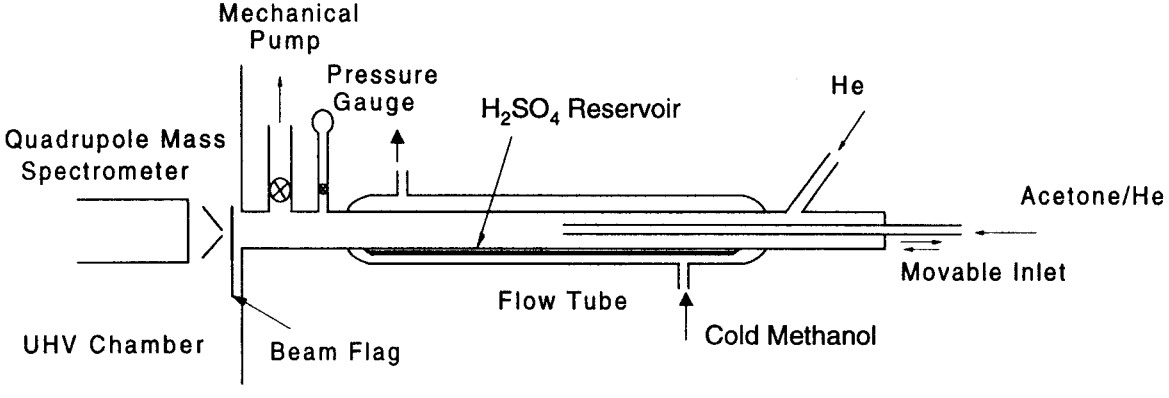

Mechanical
Pump
Pressure
Gauge
H_2SO_4 Reservoir
He
Quadrupole Mass
Spectrometer
Acetone/He
Movable Inlet
Flow Tube
Cold Methanol
UHV Chamber
Beam Flag

Fig. 1

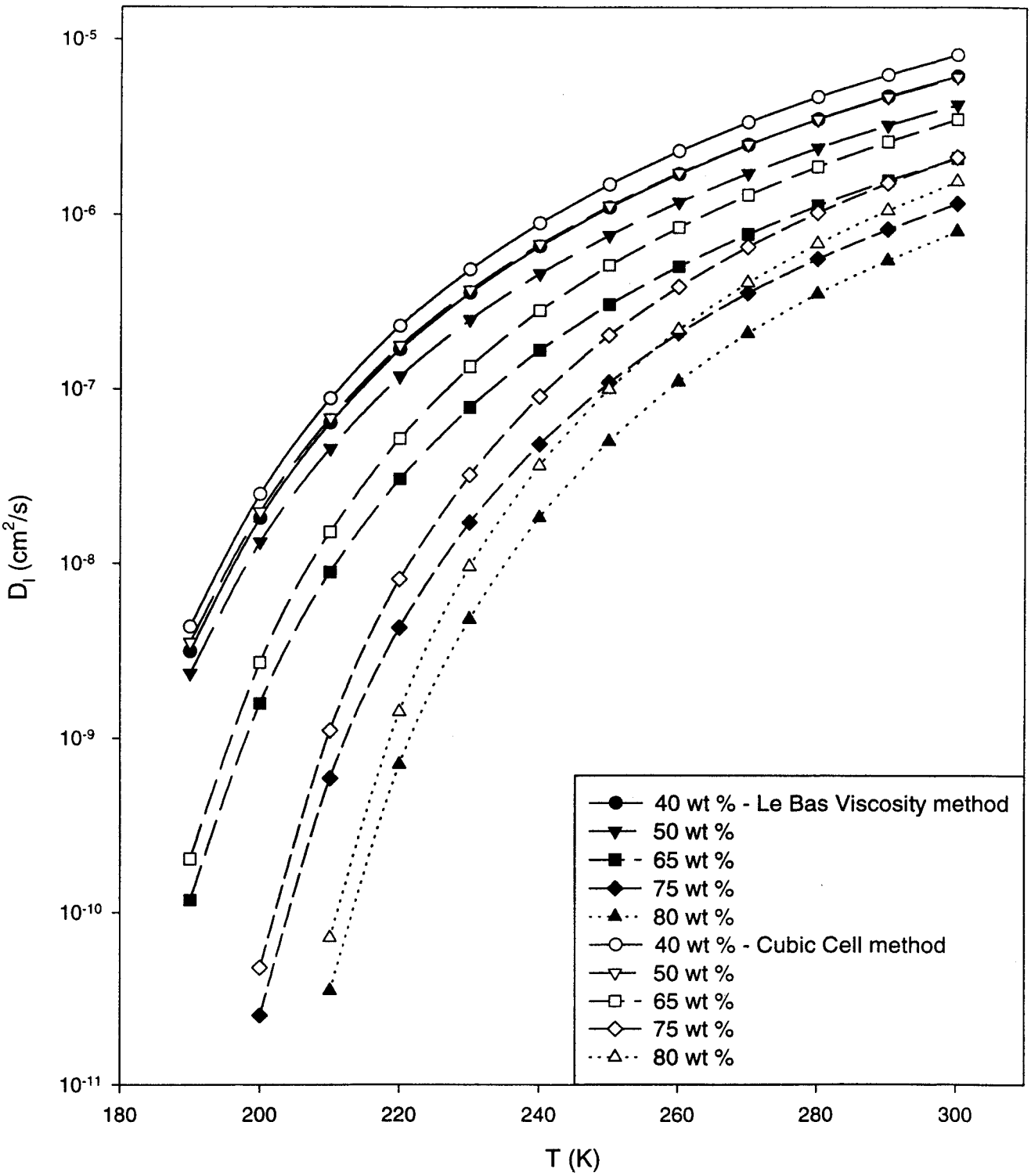

10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
D_l (cm^2/s)
180
200
220
240
260
280
300
T (K)
40 wt % - Le Bas Viscosity method
50 wt %
65 wt %
75 wt %
80 wt %
40 wt % - Cubic Cell method
50 wt %
65 wt %
75 wt %
80 wt %

Fig. 2

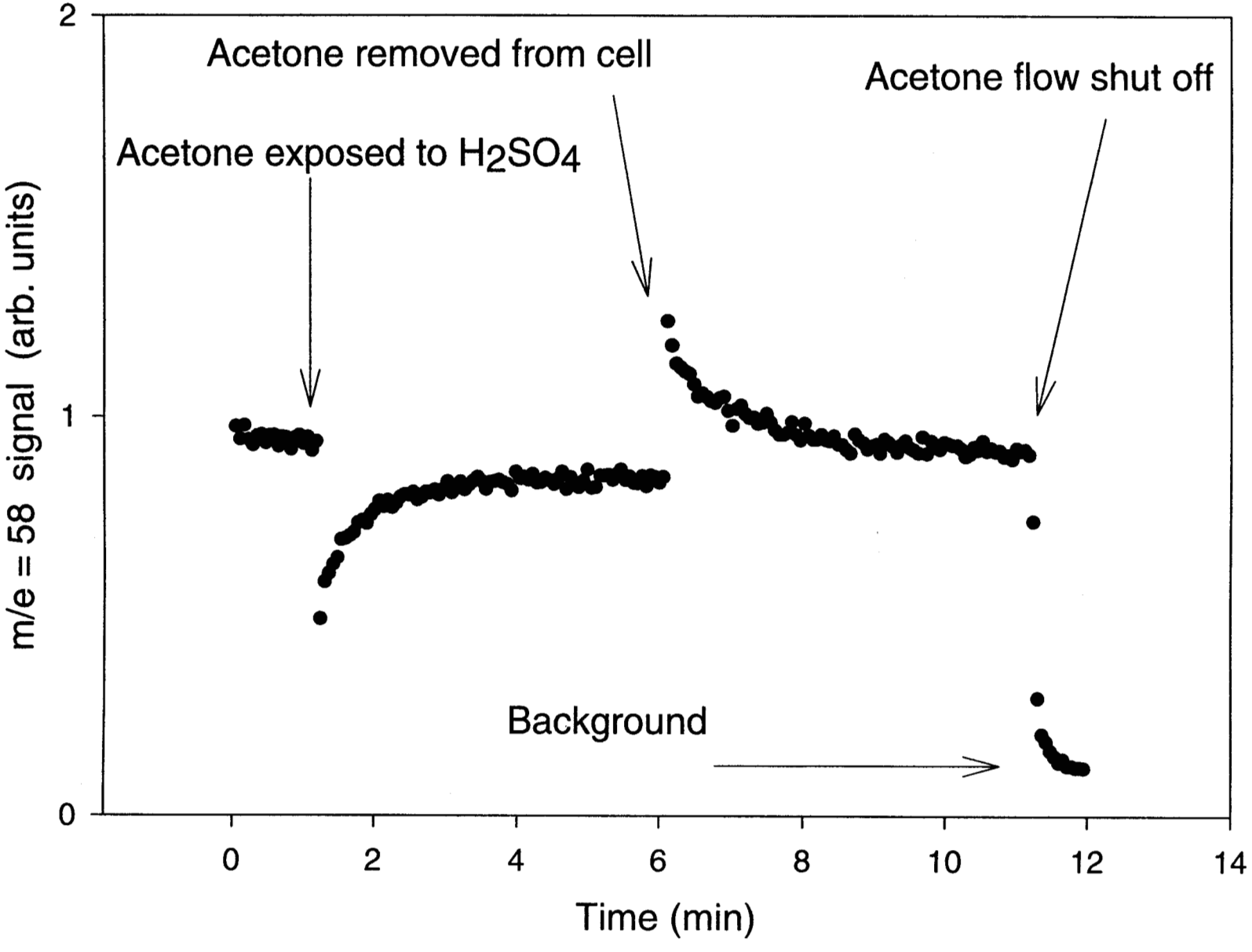
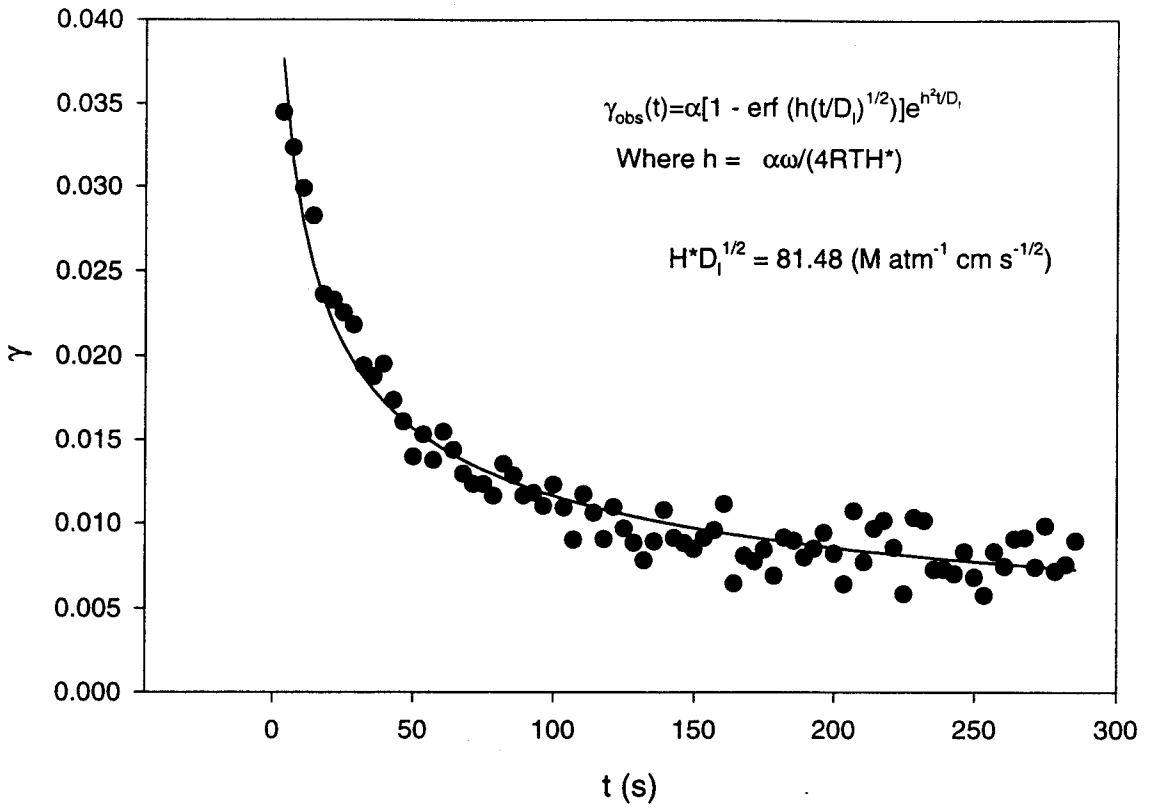

Acetone removed from cell
Acetone flow shut off
Acetone exposed to H_2SO_4
Background
m/e = 58 signal (arb. units)
Time (min)
0
1
2
0
2
4
6
8
10
12
14

Fig. 3


0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
γ
0
50
100
150
200
250
300
t (s)
$\gamma_{obs}(t)=\alpha[1 - erf (h(t/D_l)^{1/2})]e^{h^2t/D_l}$
Where h = αω/(4RTH*)
$H^*D_l^{1/2}$ = 81.48 (M atm^{-1} cm s$^{-1/2}$)

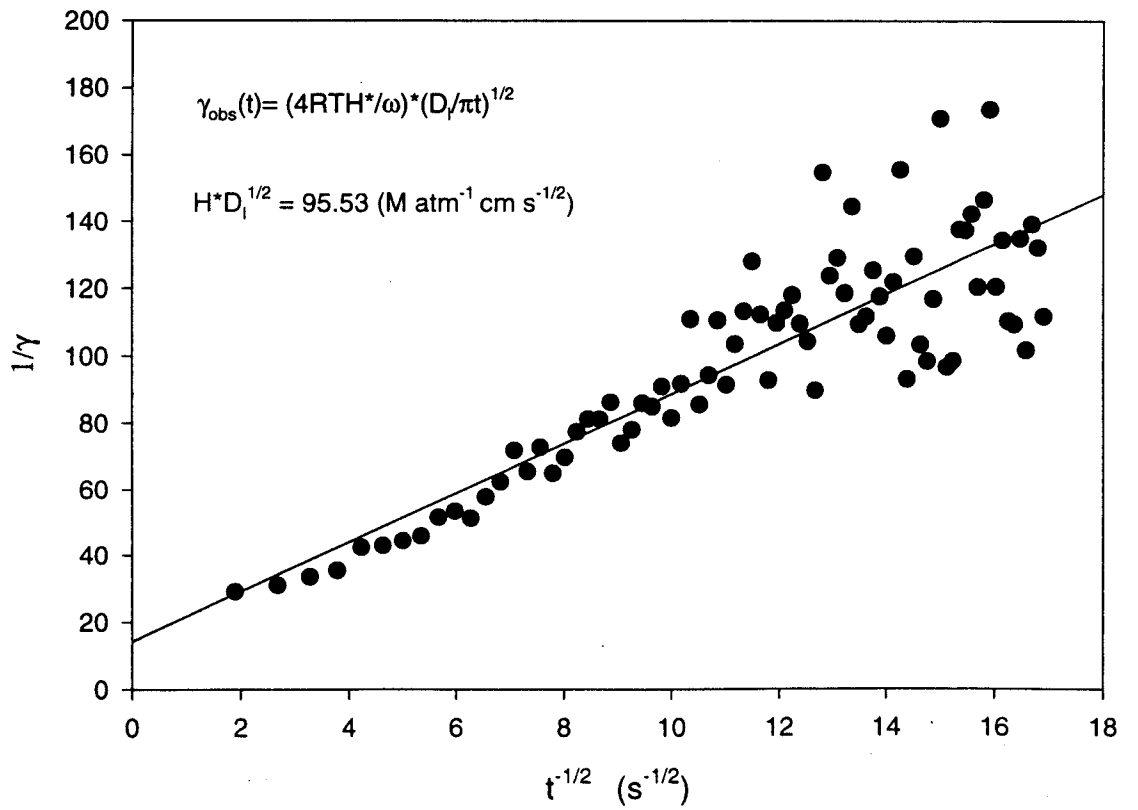

200
180
160
140
120
100
80
60
40
20
0
1/γ
0
2
4
6
8
10
12
14
16
18
$t^{-1/2}$ ($s^{-1/2}$)
$\gamma_{obs}(t)= (4RTH^*/\omega)^*(D_l/\pi t)^{1/2}$
$H^*D_l^{1/2}$ = 95.53 (M atm^{-1} cm s$^{-1/2}$)

Fig. 4

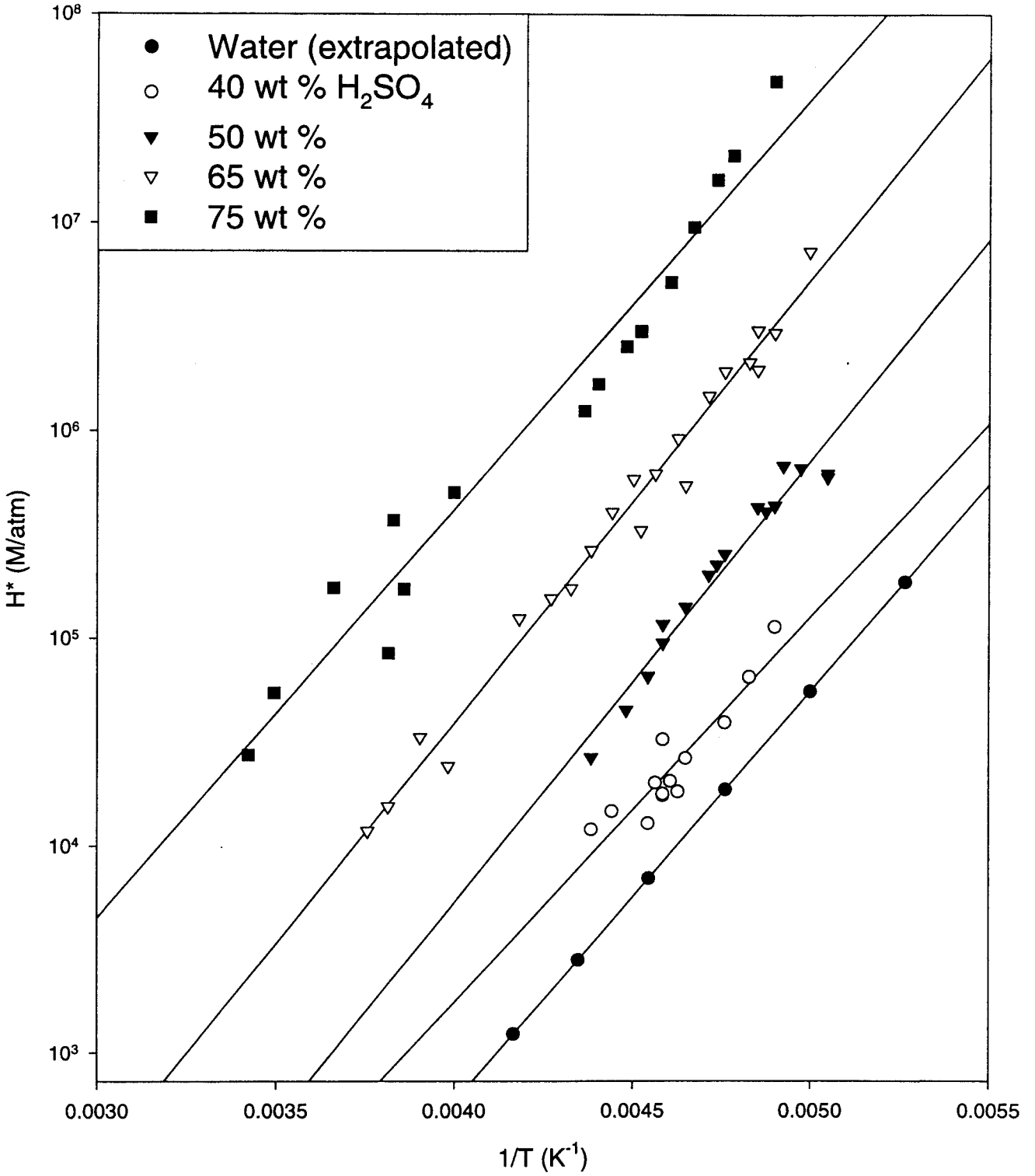

Water (extrapolated)
40 wt % H_2SO_4
50 wt %
65 wt %
75 wt %
10^8
10^7
10^6
10^5
10^4
10^3
H* (M/atm)
0.0030
0.0035
0.0040
0.0045
0.0050
0.0055
1/T (K^{-1})

Fig. 5

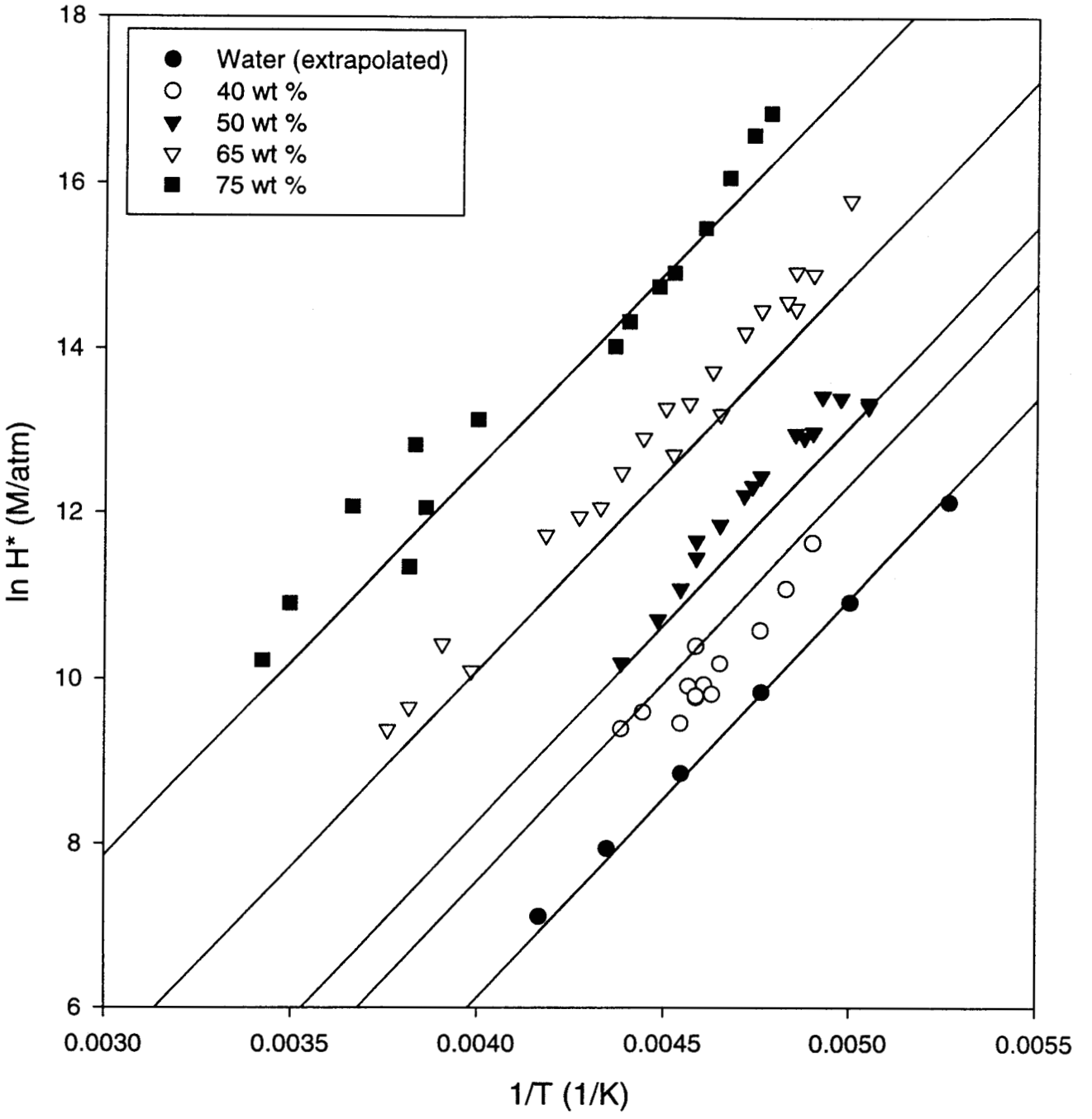
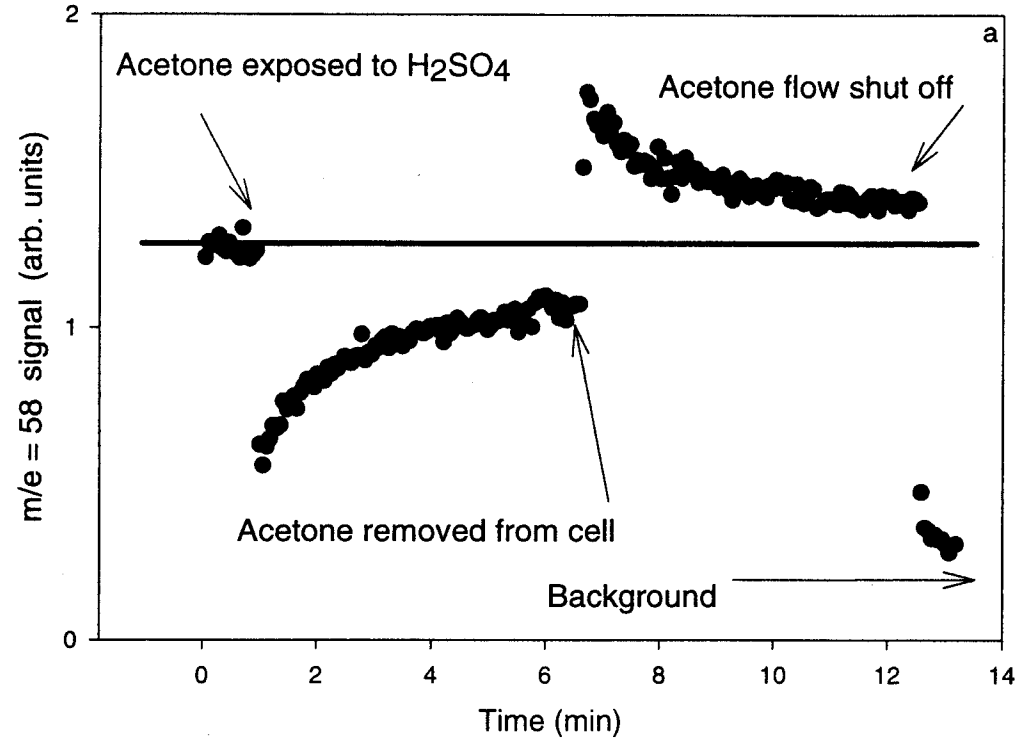

Water (extrapolated)
40 wt %
50 wt %
65 wt %
75 wt %
ln H* (M/atm)
1/T (1/K)
18
16
14
12
10
8
6
0.0030
0.0035
0.0040
0.0045
0.0050
0.0055

Fig. 6


a
Acetone exposed to H_2SO_4
Acetone flow shut off
Acetone removed from cell
Background
m/e = 58 signal (arb. units)
Time (min)
0
1
2
0
2
4
6
8
10
12
14

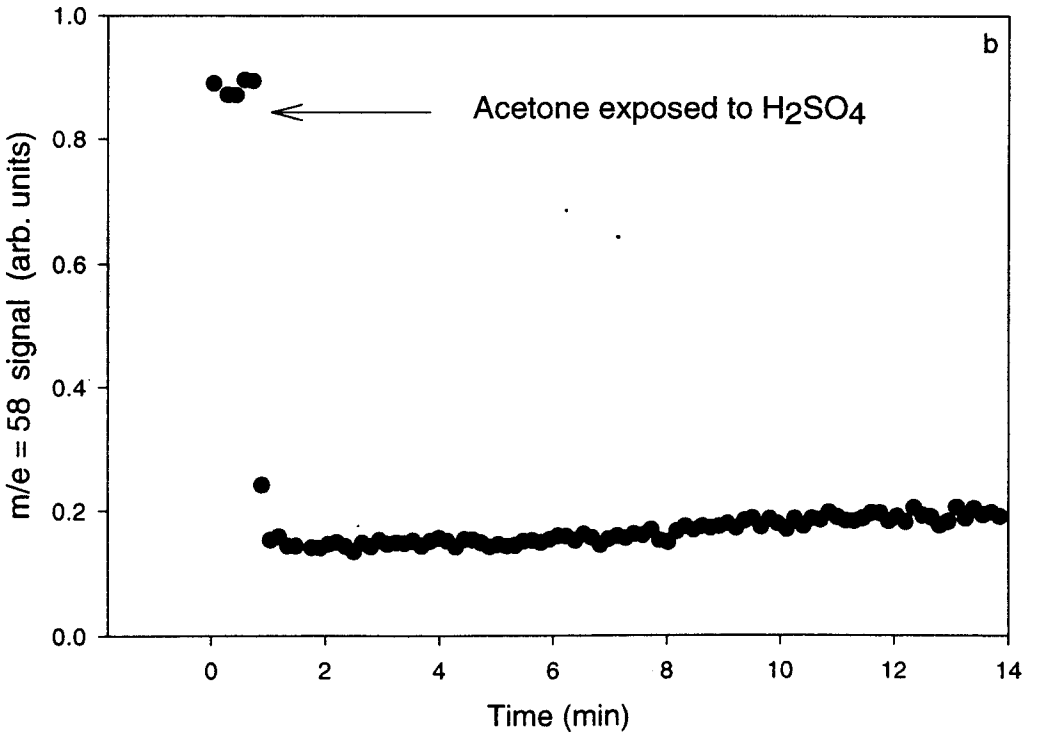

b
Acetone exposed to H_2SO_4
m/e = 58 signal (arb. units)
Time (min)
0.0
0.2
0.4
0.6
0.8
1.0
0
2
4
6
8
10
12
14

Fig. 7

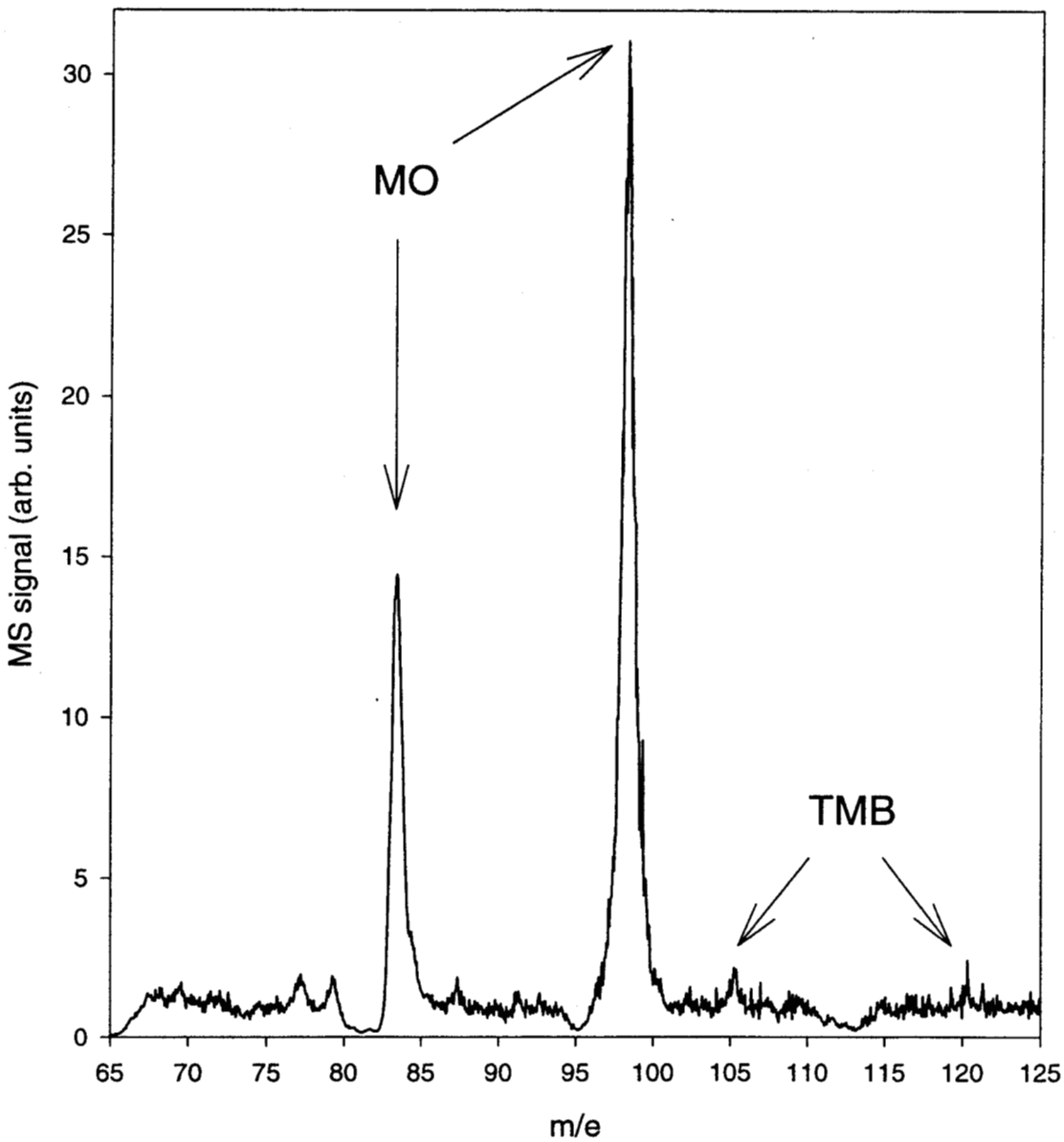

MO
TMB
MS signal (arb. units)
m/e
0
5
10
15
20
25
30
65
70
75
80
85
90
95
100
105
110
115
120
125

Fig. 8

O
CH3
CH3
H2SO4
H+
O
CH3
CH3
H2SO4
> 80 wt %
Acetone
CH3
C
OH+
C
C
CH3
CH3
H2SO4
> 87 wt %
Acetone
CH3
CH3
CH3

Fig. 9